

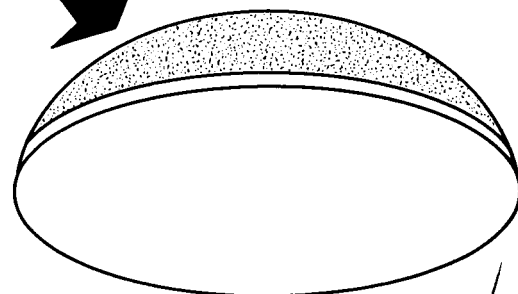
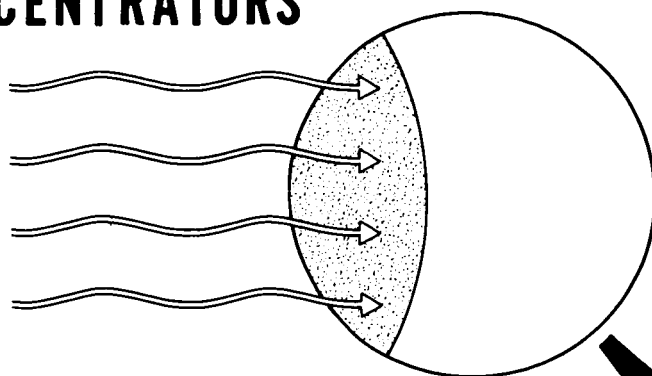
# RIGIDIZED INFLATABLE SOLAR ENERGY CONCENTRATORS

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FIRST  
QUARTERLY  
PROGRESS REPORT

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15 JANUARY 1964

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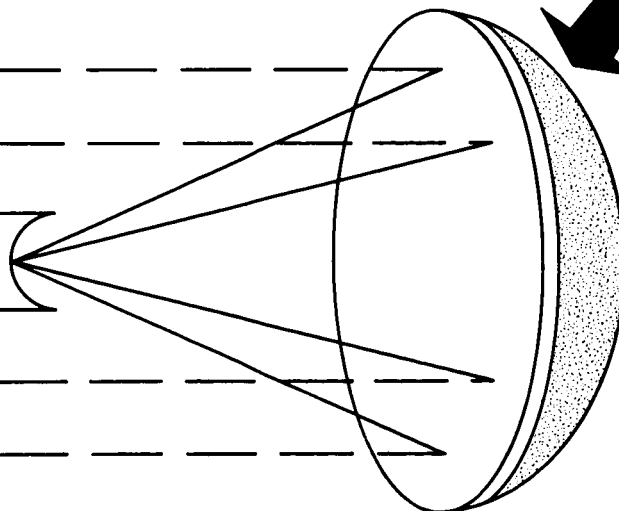
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CORPORATION

AKRON, OHIO

@ Space Systems Div.

**RIGIDIZED INFLATABLE SOLAR ENERGY  
CONCENTRATORS**

by

[ N. Jouriles and C. E. Welling ]

① First Quarterly Progress Report,  
Covering Period from 30 September 1963 through 31 December 1963  
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Langley Station  
Hampton, Virginia 23365

by

Space Systems Division  
Goodyear Aerospace Corporation  
1210 Massillon Road  
Akron, Ohio 44315

②  
HUT>

## ABSTRACT

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This first quarterly progress report covers the work accomplished from 30 September through 31 December 1963. The major areas of investigation include (1) a review of heat-activated material formulations, (2) selection of azides for evaluation, (3) contracting an azide-synthesizing firm (4) construction of test apparatus, and (5) an investigation of reactions resulting from the blending of various materials. The approach taken, the choice of materials, the measurements of experimental values, the materials under study, and the direction of future work are discussed. The azotometer analysis, the measurement of heat release from azide rearrangement, and the sublimation test are described in detail.

AUTHOR

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## SECTION I. INTRODUCTION

This first quarterly progress report covers the work accomplished from 30 September through 31 December 1963. The major areas of investigation during this report period include the following:

1. A review of heat-activated predistributed material formulations.
2. The selection of azides for synthesis and evaluation.
3. Locating and contracting an azide-synthesizing firm.
4. The investigation and construction of apparatus for screening tests.
5. The investigation of reactions resulting from the blending of various materials.

A review was made of the problem areas in predistributed rigidizing material formulations employing acid azides and polyol resins to produce heat-activated polyurethane foams in a simulated space environment. A selection was made of certain acid azide structures to be synthesized and evaluated for their suitability as predistributed rigidizing material ingredients. It was anticipated that this work would furnish guidelines for further molecular structure design and synthesis of azides best adapted to the implicit requirements of the process and foam product.

An azide-synthesizing firm was located and contracted to produce specified azide structures. Much of the experimental work accomplished up to the time of delivery of these special azides has made use of terephthaloyl azide (Structure I) prepared in the Goodyear Aerospace Corporation laboratory.

The selection of experimental procedures was made along with the design and construction of equipment where necessary to evaluate chemical and physical properties of azides and polyol resins. Among the pertinent chemical properties of the azides of interest are the rates of rearrangement to isocyanates at specified temperatures and the concurrent heat releases. A preliminary study was made of the interrelated effects of temperature and rate of foaming, initial predistributed material viscosity at foaming temperature, surfactant additions, and vacuum on the cell structure of the foam material.

At the time of the writing of this report, kinetic data and thermodynamic data are becoming available to define properties of some predistributed material formulations.

## SECTION II. GENERAL OBJECTIVE

The objective of this project is the production of a rigid polyurethane foam from ingredients that may be premixed and predistributed over a surface without reaction, by virtue of one or more ingredients being inert when mixed. The pre-distributed mixture must not react in storage and yet be capable of activation by limited heating. When activated in a vacuum environment, a low-density, high-strength foam should result.

The primary reactants in a polyurethane foam are polyesters and polyethers with reactive hydrogen in the molecule, ordinarily as pendant hydroxyl groups, and another compound having two or more isocyanate groups ( $\text{-NCO}$ ) per molecule.

The basis of the present effort is the prior finding in Goodyear Aerospace Laboratories that certain acid azides may be employed as the inert ingredient. When exposed to slightly elevated temperatures, such acid azides undergo a reaction (Curtius rearrangement of the  $\text{-CON}_3$  acid azide group to the  $\text{-NCO}$  group) that produces reactive isocyanates and also liberates molecular nitrogen that can serve as the necessary blowing gas.

Within the framework of this objective, it is necessary to search for the best choices of foam reactants and reactant ratios to yield a controllable, operable process under acceptable conditions of temperature, pressure, and time which are compatible with the environment of an earth orbit. The foam produced must in turn meet certain requirements in physical properties and compatibility with other structural components.

## SECTION III. APPROACH

## A. GENERAL

The azide approach to a predistributed rigidizing material for inflatable space structures such as solar concentrators is shown in block diagram form in Figure 1. The predistributed rigidizing material as applied to the space structure (solar concentrator) consists of an azide and a polyol resin. The reaction of the rigidizing process undergoes two steps. The first step is the heating of the azide to produce the isocyanate, and the second is the blending of the isocyanate with the polyol resin to produce the polyurethane. The resin is conditioned or advanced

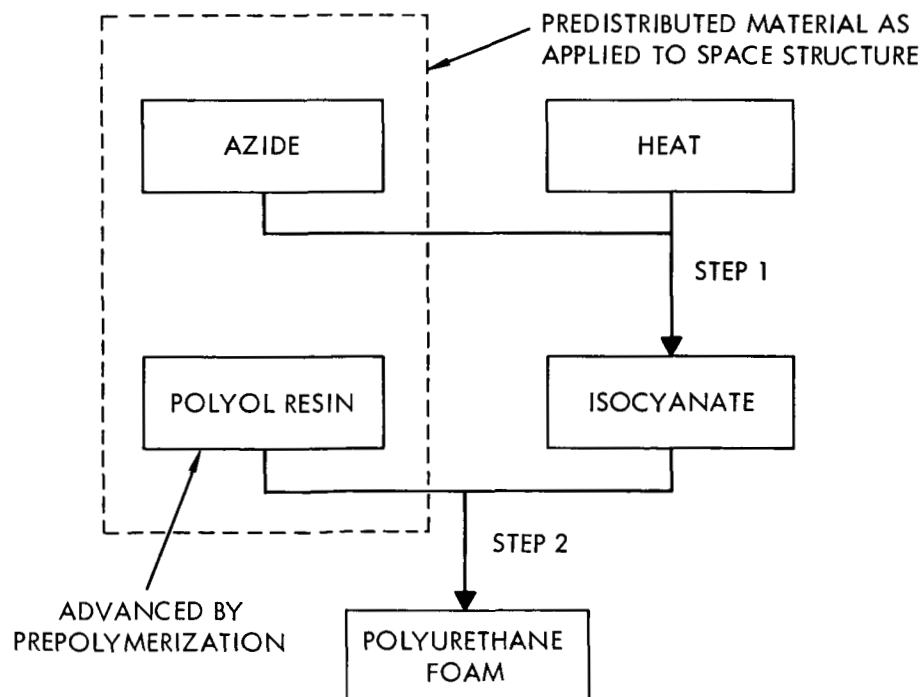


Figure 1. Block Diagram of Rigidizing Process for Predistributed Material

by prepolymerization to react readily with the isocyanate. The nitrogen gas released by the azide serves as an auxiliary blowing agent.

The predistributed material, which includes the azide and the resin, is formed into a paste and applied to Mylar (see Figure 2). The Mylar is then placed in a desiccator (Figure 3), and the desiccator is placed in an oven. The desiccator is evacuated, and the oven is heated to initiate the reaction. A biscuit of unrestrained rigidizing material is produced (Figure 4). After curing, it is dissected for inspection of the cellular structure (Figure 5).

The areas of investigation presently in view are briefly summarized in the following paragraphs. They are interrelated, but are arbitrarily classed here as related to the process or to the product.

## B. PROCESS

### 1. Choice of Azide

It is necessary that the acid azides of difunctionality or higher that are potentially useful in the process be prepared in a laboratory, since, as far as we know, none is a commercial material. The desirable properties in an azide to serve the present objective may be stated as follows:

- (1) The undergoing of the Curtius rearrangement smoothly and quantitatively in the temperature range of about 150 - 200°F in a few hours or less. A lower activating temperature is undesirable since it would create storage problems. (Various azides, mostly monofunctional, are reported in the literature to rearrange at temperatures from 60 to 300°F; side reactions may limit isocyanate yield to 80 percent or so.)

The nature of this rearrangement is as follows:

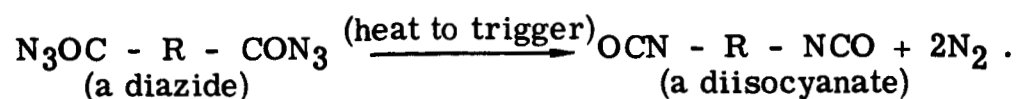




Figure 2. Sample of Predistributed Material  
Applied to Mylar



Figure 3. Sample Placed in Desiccator in Oven





Figure 4. Sample in Evacuated Desiccator in Oven  
Becomes Biscuit-Shaped

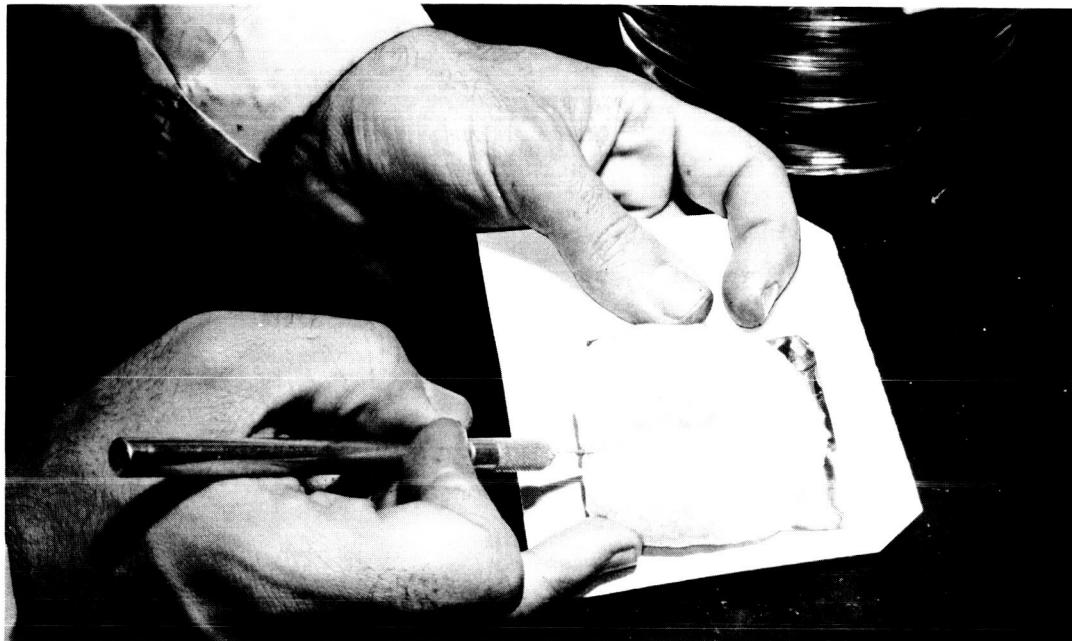


Figure 5. Dissection of Cured Biscuit

- (2) A low heat release from the rearrangement of the azide would be desired since exothermic reactions may lead into overheating.
- (3) The isocyanate resulting from the azide rearrangement should probably be a fast-reacting compound.
- (4) It is, of course, necessary to ensure the release of a sufficient amount of nitrogen blowing gas by formulating with at least a minimum amount of contained azide group per unit weight of total mixed ingredients. If larger percentages of the azide group are required to yield sufficient isocyanate for the polymerization process, the additional nitrogen release brings on complications not encountered in the usual foam systems.
- (5) Physical state at room temperature to be a liquid that would mix readily with other viscous liquid ingredients.
- (6) Very low vapor pressure of both the azide and its isocyanate rearrangement product to prevent loss of either prior to or during the foaming process.
- (7) On the basis of chemical principles and a limited number of past observations, there is some reason to believe that a part or all of the azide material could advantageously be of trifunctionality or higher.

## 2. Choice of Polyester or Polyether Resin

A considerable variety of polyether resins and a somewhat limited number of polyester resins are available from commercial sources. Properties of these materials that will affect processing include the following:

- (1) Functionality or the average number of hydroxyl groups per molecule and also molecular weight. These combined give average equivalent

weight, which is another index of structure and aids in setting up another criterion of the product, i. e., molecular weight per cross link.

- (2) The proportion between primary and secondary hydroxyl groups will affect reactivity. Primary hydroxyls would be expected to be faster reacting.
- (3) The room temperature viscosity of the resin may be expected to control the viscosity of the mixed ingredients that are to be predistributed on a film substrate. Obviously, neither very liquid nor semisolid mixtures would be desirable. The viscosity and surface tension when activation temperature is first reached will influence the early stages of foam swell.
- (4) Very low vapor pressure would be advantageous.
- (5) High solvent power for the azide co-reactant would be highly desirable if it permitted having all ingredients in a single phase.
- (6) Very low water content of these generally hygroscopic resins would be advantageous.

### 3. The Choice and Use of Auxiliary Ingredients

Auxiliary ingredients such as surface active agents and catalysts for the polymerization reaction will require consideration. We have no indication, unfortunately, that the Curtius rearrangement is susceptible to catalysis. The sensitization of acid azides to shock or temperature by impurities has been little studied, and we infer that it is not a catalytic process in the usual sense.

### C. PRODUCTS

The physical properties of strength and high softening temperature that are desired require a high density of cross links (low equivalent weights for both

isocyanate and polyol plus complete reaction).  $M_c$  values of around 500 may be desirable. ( $M_c$  = molecular weight/cross link.)

The structure of the moieties between cross links will be determined, of course, by the structures of the azides and polyol reactants. Indications are that azides containing a high percentage of aromatic rings will contribute to a stiff polymeric structure. Likewise, in the polyol (polyester or polyether resin), the aromatic or heterocyclic character may be advantageous.

## SECTION IV. AZIDE RESEARCH

## A. GENERAL

Table I summarizes information on azides studied to date. Structures I through V were prepared by Goodyear Aerospace in an in-house development program. Efforts were under way to synthesize Structure VI when the contract was let to Goodyear Aerospace. Continuing efforts have not yet been successful. Structures X, XI, and XII were contracted for, and partial deliveries were received in December 1963. Product quality and purity is probably good (not yet completely established) for Structures X and XI. The product from attempts to prepare Structure XII was submitted for our interest, but is known to be at least quite impure. The availability of Structure I through our own synthesis efforts and our experience with it in predistributed material formulations has led to using it in development of techniques as a reference or guinea pig.

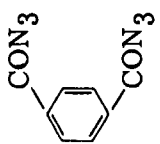
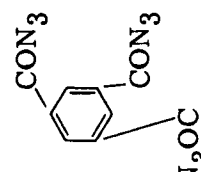
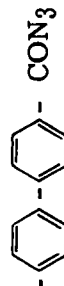
## B. MEASUREMENT OF EXPERIMENTAL VALUES (See Table I)

The density of azides was determined on powdered samples with a Bechman Air pycnometer and is the crystal density (not bulk density).

The melting point was determined on a melting point bar or with a polarizing microscope and Kofler hot stage.

Values for half life in minutes at stated temperature were derived from preliminary runs with an azotometer in which the rearrangement of an azide sample was effected and the concomitant release of nitrogen measured as a function of time. The azotometer technique is described in Appendix A.

Table I. Properties of Acid Azides

| Structure | Azide Name<br>and Mol Structure   | Azide<br>Function-<br>ality | Isocyanate<br>Produced<br>on Re-<br>arrangement                          | Azide N<br>Content<br>(Wt %) |            | Azide<br>Melting<br>Point<br>(°F)    | Crystal<br>Density<br>of Azide<br>(g/cc) | Half Life**<br>at Stated<br>Temperature<br>(min) | Heat Release on<br>Rearrangement<br>at 275°F<br>(cal/g) | Remarks<br>Pertaining<br>to Azides   |
|-----------|---|-----------------------------|--|------------------------------|------------|--------------------------------------|--|--|---|--|
|           |   |                             |  | Total                        | Releasable |                                      |  |  |   |  |
| I*        | Terephthaloyl<br>Azide<br><br>Mol wt = 216     | 2                           | 1, 4-Benzene<br>Diisocyanate<br>Mol wt = 160<br>Amine eq = 80            | 38.9                         | 25.9       | 230 -<br>232                         | 1.58                                     | 30 - 40 (prelim)<br>at 196°F                     | 282   | Shock sensitive.<br>Heat sensitive.<br>~one percent/<br>month decom-<br>position at<br>70°F. |
| II*       | Mesoyl (tri) Azide<br><br>Mol wt = 285       | 3                           | 1, 3, 5-Benzene<br>Triisocyanate<br>Mol wt = 201<br>Amine eq = 67        | 44.2                         | 29.5       | 174                                  | --                                       | --   | --  | Extremely<br>shock sensitive.  |
| III*      | Sebacoyl Azide<br>N3OC (CH2)8CON3<br>Mol wt = 252   | 2                           | Octamethylene<br>Diisocyanate<br>Mol wt = 196<br>Amine eq = 98           | 33.3                         | 22.2       | ~75<br>(litera-<br>ture<br>value 93) | --                                       | --   | --  | Noticeably<br>thermally un-<br>stable at 75°F.   |
| IV*       | 4, 4'-Diphenoyl<br>Azide<br><br>Mol wt = 292 | 2                           | 4, 4'-Biphe-<br>nylene<br>Diisocyanate<br>Mol wt = 236<br>Amine eq = 118 | 29.8                         | 19.2       | 259                                  | --                                       | --   | --  | Perhaps too<br>thermally<br>stable. Di-<br>isocyanate is<br>a known<br>carcinogen.           |

\*First synthesized and studied on Goodyear Aerospace in-house development program.

\*\*Assuming a unimolecular reaction, the time for 50 percent of the material to undergo rearrangement as measured by nitrogen release.

Table I. Properties of Acid Azides (Continued)

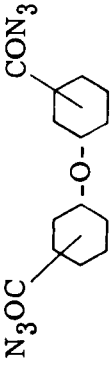
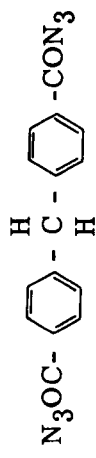

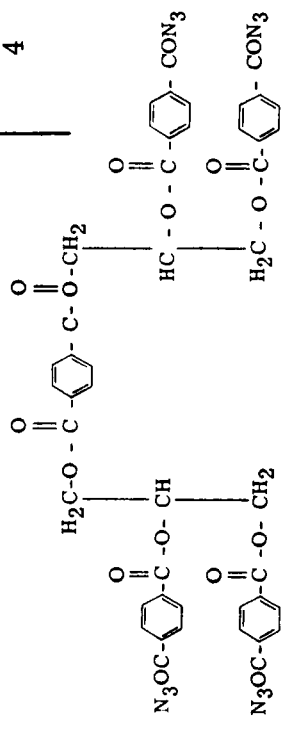
| Structure | Azide Name<br>and Mol Structure   | Azide<br>Function-<br>ality | Isocyanate<br>Produced<br>on Re-<br>arrangement  | Azide N<br>Content<br>(Wt %) |            | Azide<br>Melting<br>Point<br>(°F) | Crystal<br>Density<br>of Azide<br>(g/cc) | Half Life**<br>at Stated<br>Temperature<br>(min) | Heat Release on<br>Rearrangement<br>at 275°F<br>(cal/g) | Remarks<br>Pertaining<br>to Azides |
|-----------|---|-----------------------------|--|------------------------------|------------|-----------------------------------|--|--|---|------------------------------------|
|           |   |                             |  | Total                        | Releasable |                                   |  |  |   |                                    |
| V*        | 4, 4'-Diacyl Azide<br>of Ethylene Glycol<br>Dibenzoate<br><br>$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{O}-\text{C}-\text{C}_6\text{H}_4-\text{CON}_3 \\   \\ \text{O} \\ \parallel \\ \text{C}-\text{O}-\text{C}-\text{C}_6\text{H}_4-\text{CON}_3 \end{array}$ Mol wt = 404 | 2                           | 4, 4'-Diisocyanate of<br>Ethylene Glycol<br>Dibenzoate<br><br>Mol wt = 348<br>Amine eq = 174 | 20.8                         | 13.9       | --                                | --                                       | --   | --  | Purity uncertain.                  |
| VI        | 2, 6-Naphthaloyl<br>Azide<br><br>$\begin{array}{c} \text{CON}_3 \\   \\ \text{C}_6\text{H}_3 \\   \\ \text{N}_3\text{OC} \end{array}$ Mol wt = 266  | 2                           | 2, 6-Naphthalene<br>Diisocyanate<br><br>Mol wt = 210<br>Amine eq = 105                       | 31.5                         | 21.1       | --                                | --                                       | --   | --  | Synthesis incomplete.              |
| VII†      | Adipoyl Azide<br>$\text{N}_3\text{OC}(\text{CH}_2)_4\text{CON}_3$<br>Mol wt = 196   | --                          | --   | 42.8                         | 28.6       | --                                | --                                       | --   | --  | --                                 |
| VIII†     | 3, 3'-Dimethoxy,<br>4, 4'-Diphenoyl Azide<br><br>$\begin{array}{c} \text{H}_3\text{C}-\text{O} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{N}_3\text{OC}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_3 \\   \\ \text{CON}_3 \end{array}$ Mol wt = 352  | --                          | --   | 23.9                         | 15.9       | --                                | --                                       | --   | --  | --                                 |

\*First synthesized and studied on Goodyear Aerospace in-house development program.

\*\*Assuming a unimolecular reaction, the time for 50 percent of the material to undergo rearrangement as measured by nitrogen release.

†Preparation of this structure contemplated during the Goodyear Aerospace in-house development program.

Table I. Properties of Acid Azides (Continued)

| Structure | Azide Name<br>and Mol Structure   | Azide<br>Function-<br>ality | Isocyanate<br>Produced<br>on Re-<br>arrangement                            | Azide N<br>Content<br>(Wt %) |            | Azide<br>Melting<br>Point<br>(°F) | Crystal<br>Density<br>of Azide<br>(g/cc) | Half Life**<br>at Stated<br>Temperature<br>(min) | Heat Release on<br>Rearrangement<br>at 275°F<br>(cal/g) | Remarks<br>Pertaining<br>to Azides                          |
|-----------|---|-----------------------------|--|------------------------------|------------|-----------------------------------|--|--|---|---|
|           |   |                             |  | Total                        | Releasable |                                   |  |  |   |   |
| IX†       | Di-Acyl Azide of<br>Oxy-Dibenzoic Acid<br><br>Mol wt = 308     | --                          | --   | 27.3                         | 18.2       | --                                | --                                       | --   | --  | --  |
| X         | 4,4'-Diphenyl<br>Methane Diacyl<br>Azide<br><br>Mol wt = 306 | 2                           | 4,4'-Diphenyl<br>Methane<br>Diisocyanate<br>Mol wt = 250<br>Amine eq = 125 | 27.4                         | 18.3       | --                                | 1.34                                     | 30 (prelim)<br>at 193°F                          | --  | Have not ob-<br>served de-<br>tonation on<br>rapid heating. |
| XI        | <br>Mol wt = 464   | 2                           | --<br>Mol wt = 408<br>Amine eq = 204                                       | 18.1                         | 12.1       | --                                | 1.31                                     | 30 (prelim)<br>at 196°F                          | --  | Have not ob-<br>served de-<br>tonation on<br>rapid heating. |
| XII       | <br>Mol wt = 1006  | 4                           | --<br>Mol wt = 894<br>Amine eq = 224                                       | 16.7                         | 11.1       | --                                | --                                       | --   | --  | No authentic<br>material yet<br>available.                  |

\*\*Assuming a unimolecular reaction, the time for 50 percent of the material to undergo rearrangement as measured by nitrogen release.  
† Preparation of this structure contemplated during the Goodyear Aerospace in-house development program.



The heat release (calories/gram of azide) for the rearrangement of azide to isocyanate is determined by rapid decomposition in a simple calorimeter at usually 275°F. This technique is described in Appendix B.

### C. CONSIDERATION OF MOLECULAR STRUCTURE VERSUS PROPERTIES OF AZIDE STRUCTURES

The objectives to be realized with the synthesis of Structures X, XI, and XII are as follows:

- (1) The azide structures form a series with increasing molecular weights. Thus the molecular weights for Structures I, X, XI, and XII are 216, 306, 464, and 1006 respectively. It is hoped that the vapor pressure and the tendency to sublime in vacuum, which has been troublesome with Structure I, will be sufficiently reduced somewhere along the series of increasing molecular weight.
- (2) It will be noted from Table I that there is a progressively decreasing nitrogen content through the sequence of Structures I, X, XI, and XII. It is expected that the explosive characteristic will be lost in progressing from Structure I to XII.
- (3) The product of the rearrangement of Structure I, namely 1,4-benzene diisocyanate or I-1, while structurally similar to the much commercially used tolylene diisocyanate (TDI), is free of the steric hindrance factor caused by the methyl group on TDI. Hence I-1 is probably somewhat faster reacting than TDI under like conditions. In designing Structures X, XI, and XII, it was thought desirable to maintain a parallel situation with Structure I by avoiding steric hindrances and allowing only 1,4- (para) substitutions on benzene rings carrying the -CON<sub>3</sub> precursors of the isocyanate groups. The freedom from steric

hindrance and probability of maximum reactivity of the isocyanate groups may be particularly desirable as molecular mobility is reduced by increased molecular weight. It may be noted that Structure X has additional utility in that it rearranges to a well known and available compound, 4,4'-diphenyl methane diisocyanate (MDI). This may permit correlations with existing polyurethane technology.

- (4) Structures X, XI, and XII are designed with high aromatic ring content on the basis of the generally established utility of aromatic isocyanates and aromatic polyesters for rigid foams with good heat distortion resistance. The superiority of aromatic diisocyanates over polymethylene diisocyanates in forming rigid urethanes seems well established in the literature.\* Aromatic rings other than benzene, naphthenic rings, and heterocyclic rings might well be considered, however, for the backbone of azide structures.
- (5) In considering the design of Structures X, XI, and XII to have a suitable degree of thermal instability, there were no very positive correlations of molecular backbone structure and thermal instability of attached  $-\text{CON}_3$  groups for guidance. However, the preliminary evaluations indicate that Structures X and XI have useful rates of thermal decomposition, of the same order as Structure I. The complexity of the situation is indicated by the fact that Structure IV is quite similar to Structure X, but was found in early Goodyear Aerospace studies to be somewhat too stable to be a promising candidate material.

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\*See, for example, "High Polymers," Vol XVI, Part I, pp 261-346, Saunders and Frisch, Interscience, 1962.

SECTION V. POLYOL RESINS AND PARTIAL  
PREPOLYMERS UNDER STUDY

The properties of commercial and experimental resins and the derived partial prepolymers are listed in Table II. It is desired to determine the utility of polyols having some of the following characteristics:

- (1) Selected molecular structure contributing resistance to heat distortion. Heterocyclic polyether structures are represented by RS-375 and HP-370; an aromatic polyester structure is available in PFR-6.
- (2) Medium to high functionality, medium to low equivalent weight per hydroxyl group, and principally primary hydroxyls. These factors should afford suitably high density of cross links and maximum speed of reaction with isocyanate.
- (3) Viscosity at projected foaming temperatures (approx 175°F) in the range of 10,000 centipoise upwards. The desirability of high viscosity is dependent upon its having a favorable influence upon foam cell structure. It would also allow preliminary building of molecular weight to a higher level and the need for less azide in the final foaming step. While minimum surface tension is desirable, this property will be controlled by an added surfactant, rather than by structure of the resin.

Table III is assembled to show weight relationships when azide structures I, X, and XI are reacted with the individual polyol resins. In each case, chemical equivalents of isocyanate (from azide) and hydroxyl are taken. This would maximize physical properties that are dependent upon cross linking. Some other factors are shown which may be calculated once the stoichiometry is fixed, such as

Table II. Properties of Polyol Resins and Partial Prepolymers

| Plaskon PFR-6 (An Aromatic Polyester) |                      |                 |
|---------------------------------------|----------------------|-----------------|
| Property                              | Manufacturer's Data  | Lab Measurement |
| Acid No.                              | 15-20                | 14              |
| Hydroxyl No.                          | 465 - 495            | 538             |
| Brookfield Viscosity at 77°F          | 70, 000 - 80, 000 cp | 65, 500 cp      |
| Water Content                         | 0. 0 - 0. 4 percent  | 0. 83 percent   |
| Density                               | --                   | 1. 15 g/cc      |

| Glidfoam RCR 5043     |                     |                 |
|-----------------------|---------------------|-----------------|
| Property              | Manufacturer's Data | Lab Measurement |
| Amine Equivalent      | 123:1               | 126             |
| Hydrolyzable Chlorine | 0. 009              | --              |
| Density               | --                  | 1. 21 g/cc      |

| Prepolymer from 10 pbw PFR-6 + 2. 3 pbw Glidfoam RCR 5043 |             |
|---|-------------|
| Property  | Measurement |
| Brookfield Viscosity at 194°F                             | 49, 500 cp  |
| Brookfield Viscosity at 212°F                             | 25, 000 cp  |
| Brookfield Viscosity at 230°F                             | 14, 000 cp  |
| Density   | 1. 2 g/cc   |

| Prepolymer from 10 pbw PFR-6 +2. 8 pbw Glidfoam RCR 5043 |              |
|--|--------------|
| Property   | Measurement  |
| Brookfield Viscosity at 194°F                            | >100, 000 cp |
| Brookfield Viscosity at 212°F                            | 85, 000 cp   |
| Brookfield Viscosity at 230°F                            | 55, 000 cp   |
| Brookfield Viscosity at 284°F                            | 8, 500 cp    |
| Density  | 1. 18 g/cc   |

Table II. Properties of Polyol Resins and Partial Prepolymers (Continued)

| Voranol RS-375 (a Sucrose-Based Polyether)  |                     |                 |
|---|---------------------|-----------------|
| Property                                    | Manufacturer's Data | Lab Measurement |
| Acid No.                                    | 3.9                 | --              |
| Hydroxyl No.                                | 375                 | --              |
| Equivalent weight                           | 151                 | --              |
| Functionality                               | 8                   | --              |
| Density                                     | --                  | 1.14 g/cc       |
| Brookfield Viscosity at 74°F                | ~38,000 cp          | 47,000 cp       |
| Brookfield Viscosity at 180°F               | 290 cp              | --              |
| HP-370 (a Methyl Glucoside-Based Polyether) |                     |                 |
| Property                                    | Manufacturer's Data | Lab Measurement |
| Equivalent Weight                           | ~150                | --              |
| Functionality                               | 4                   | --              |
| Brookfield Viscosity at 76°F                | --                  | 27,500 cp       |
| Density                                     | --                  | 1.12 g/cc       |

quantity of blowing gas released and adiabatic temperature rise from azide rearrangement. The heat releases indicated show the desirability of reducing the azide component as much as resultant modification of physical properties will permit while attempting to operate the foaming process as nearly isothermally as possible.

Experimental foaming studies have been made principally with Table III formulation components, but at lower azide concentrations. We have observed some improvement in foam cell structure by use of silicone additions, but there is also loss in rigidity. Further work will be done with several new silicones and at higher azide levels. Attempts have been made to evaluate the utility of silicones

## SECTION V

Table III. Relationships in Formulating Azides with Polyol Resins

| Resin  | PFR-6 (Hydroxyl No. = 480) |                   |                   | Voranol RS-375<br>(Hydroxyl No. = 375) |                   |                       | HP-370<br>(Hydroxyl No. = 370) |                   |                   | Prepolymer from<br>10 pbw PFR-6 +<br>2.3 pbw Glidfoam RCR-5043<br>(Hydroxyl No. = ~304) |                  |                   |
|--|----------------------------|-------------------|-------------------|--|-------------------|-----------------------|--------------------------------|-------------------|-------------------|---|------------------|-------------------|
|  | 100(pbw)                   | 100(pbw)          | 100(pbw)          | 100(pbw)                               | 100(pbw)          | 100(pbw)              | 100(pbw)                       | 100(pbw)          | 100(pbw)          | 100(pbw)  | 100(pbw)         | 100(pbw)          |
| Azide Component (for<br>-NCO/OH = 1)                                   |                            |                   |                   |  |                   |                       |                                |                   |                   |   |                  |                   |
| Structure I  | $\frac{92}{192}$           | --                | --                | $\frac{71.5}{171.5}$                   | --                | --                    | $\frac{72}{172}$               | --                | --                | $\frac{58}{158}$  | --               | --                |
| Structure X  | --                         | $\frac{131}{231}$ | --                | --                                     | $\frac{101}{201}$ | --                    | --                             | $\frac{102}{202}$ | --                | --  | $\frac{83}{183}$ | --                |
| Structure XI   | --                         | --                | $\frac{198}{298}$ | --                                     | --                | $\frac{153.5}{253.5}$ | --                             | --                | $\frac{155}{255}$ | --  | --               | $\frac{125}{225}$ |
| Weight after Azide<br>Rearrangement                                    | 168                        | 207               | 274               | 153                                    | 182.5             | 235                   | 153                            | 183               | 236               | 143   | 168              | 210               |
| Calculated Mol Wt<br>/Cross Link ( $M_c$ )                             | †                          | †                 |                   | 308                                    | 367               | 473                   | 459                            | 549               | 708               | †   | †                | †                 |
| Vol N <sub>2</sub> (STP)/Vol<br>Polyurethane Solids<br>(Calculated)*   | 136                        | 111               | 84                | 116                                    | 97                | 76                    | 119                            | 100               | 77                | 102   | 87               | 69                |
| Adiabatic Temp Rise from<br>Azide Rearrangement - °F<br>(Calculated)** | 617                        | --                | --                | 528                                    | --                | --                    | 532                            | --                | --                | 457   | --               | --                |

\*Assuming for polyurethane solids,  $d = 1.2$  g/cc

\*\*Based on a heat release of 282 cal/g for Structure I, material weight after rearrangement, and material specific heat of 0.45 cal/g-°C assumed.

† Information on average functionality of PFR-6 is not available at present.

by observing their stabilizing influence on mechanically produced froths of polyol resins and partial prepolymers. This approach has not indicated stabilizing ability when used with PFR-6 partial prepolymer at 175°F, although marked stabilization can be effected with other resins at room temperature and at about the same viscosity level.

Froth stabilization is deemed desirable to offset drainage from cell walls and bubble coalescence during the extended periods of foam generation.

## SECTION VI. DIRECTION OF FUTURE WORK

An evaluation will be made of polyurethane polymers from polyisocyanates that are derived from the azides and the various candidate polyols. (Vicat softening tests will serve as a guide.) Studies will be made of the foaming process and the use of surfactants and their relationships to the cell structure of the product.

Work will be continued to study formulation variations and their effect upon polymer strength and temperature dependence of strength. This will include use of various polyols.

Evaluation methods for new azides will be pursued. The areas of investigation will include:

- (1) Determination of shock sensitivity (and friction sensitivity).
- (2) Thermal decomposition characteristics, time versus temperature.
- (3) Heat release on decomposition as determined by calorimetry.
- (4) Solubility in solvents and in prepolymer.
- (5) Sublimation tendency in high vacuum.
- (6) Test formulations made with consideration of:
  - (a) Balance between -OH and produced -NCO.
  - (b) Available releasable nitrogen for blowing.
  - (c) Azide decomposition rate, urethane reaction rate, and viscosity when blowing.

These areas are to be evaluated in terms of density, foam polymer melt temperature (PMT), heat effects, cell structure, post-cure, and distortion.



## APPENDIX A. AZOTOMETER TEST AND ANALYSIS

The azotometer\*(similar to a nitrometer) apparatus is shown in Figures 6 and 7. It is used to measure the volume of nitrogen evolved during the rearrangement of an organic compound, the azide material. A description of its operation follows.

One hundred milligrams of azide material and 0.5 to 1.0 gram of unreactive paraffin oil (for heat transfer) are placed in the bottom of the reaction tube. The gas burette contains a potassium hydroxide solution with a layer of mercury at the bottom extending to about one-half inch above the entrance tube. The system is already purged with CO<sub>2</sub>, and the CO<sub>2</sub> is allowed to flow continuously at a rate of approximately one bubble per second or 5 cc/minute. Blank runs are made to determine the volume of insoluble gas collected; this represents impurities in the CO<sub>2</sub>.

The sample of azide placed in the reaction tube is maintained at room temperature until the start of the run, which is initiated by raising a preheated, thermostated water bath around the reaction tube. Nitrogen gas, which then begins to be evolved by the azide, is swept in the flowing CO<sub>2</sub> stream to the gas collection burette, and there its rate of collection versus time is observed. Appropriate corrections for temperature, barometric pressure, and water vapor over the KOH solution are made to the nitrogen volume. The amount of nitrogen evolved is determined by the following calculation:

$$N = \left( \frac{V}{22,400} \right) \frac{N_{MW} \times 100}{S_W}, \quad (1)$$

\*S. Siggia, "Quantitative Organic Analysis via Functional Groups," Third Edition. John Wiley and Sons, Inc, New York, 1963, p 545.  $\alpha$

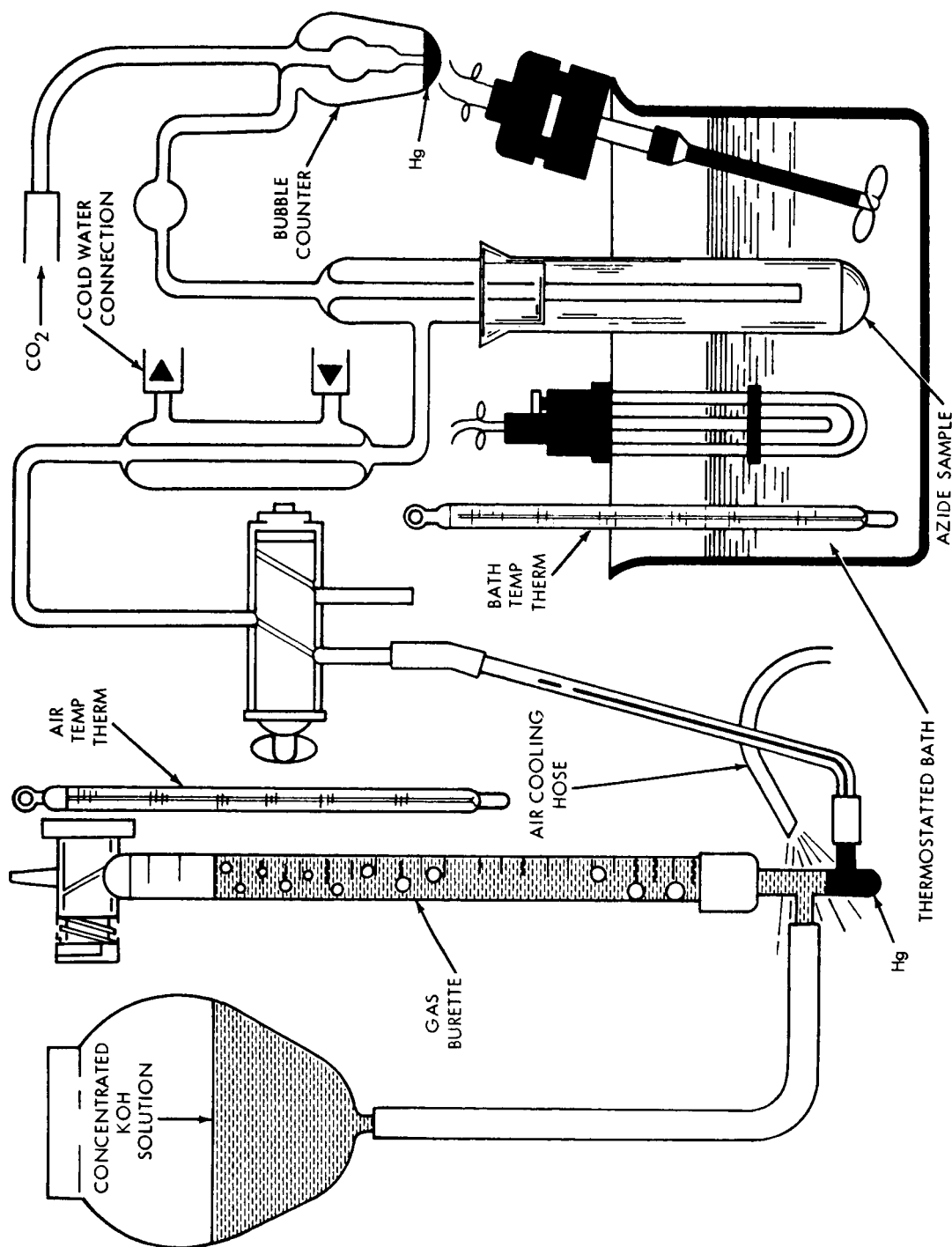


Figure 6. Sketch of Azotometer Apparatus

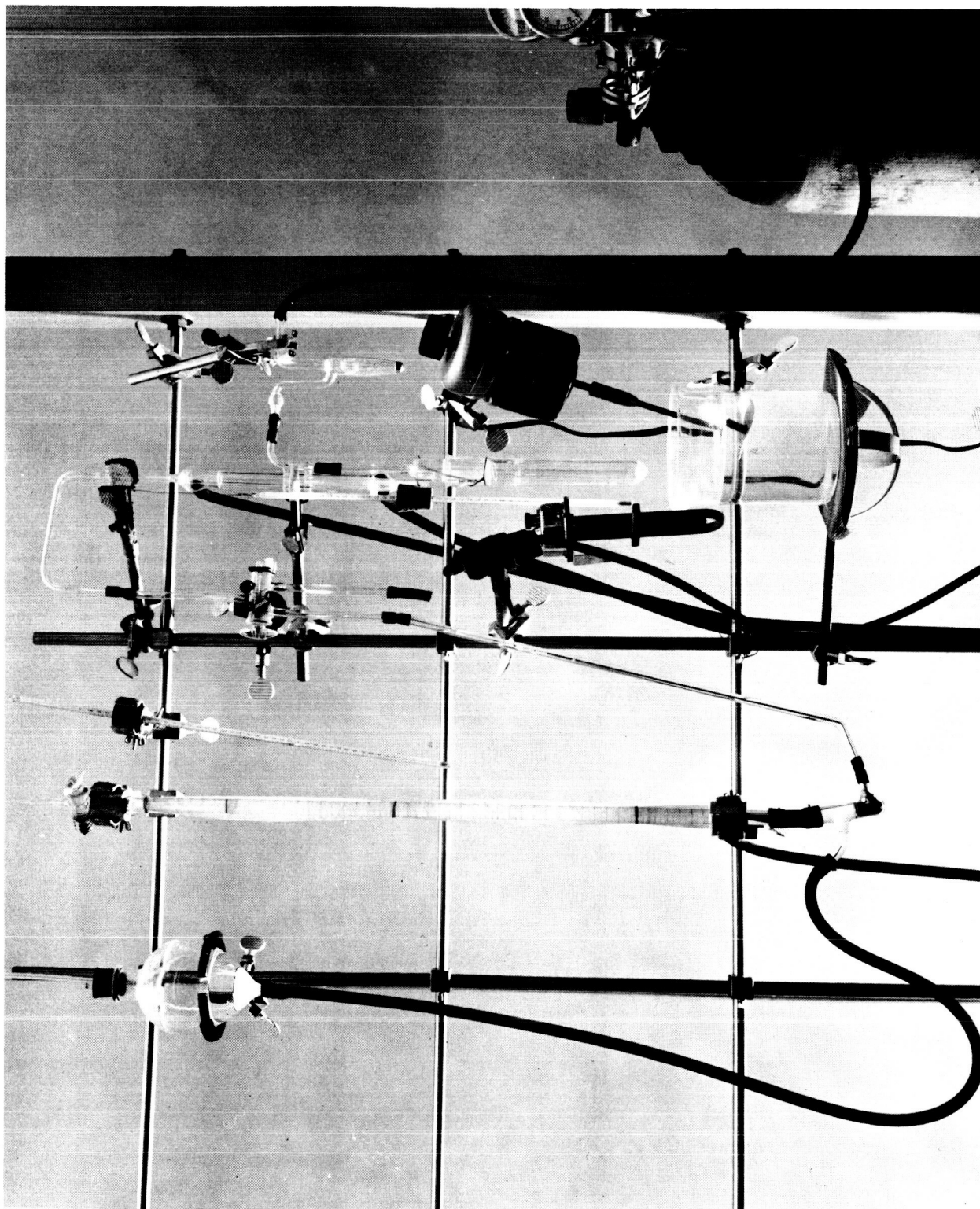


Figure 7. Photograph of Azotometer Apparatus

## APPENDIX A. AZOTOMETER TEST AND ANALYSIS

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where

$N$  = amount of nitrogen evolved in percent of azide compound by weight,

$V$  = volume of gas collected - corrected for  $\text{CO}_2$  blank and for NTP in  $\text{cm}^3$ ,

$N_{\text{MW}}$  = molecular weight of the nitrogen,

$S_{\text{W}}$  = weight of the azide sample in gms.

The determination is accurate and precise to better than  $\pm 1$  percent.

Azotometer information gives the rate and amount of nitrogen evolved when the azide is exposed to a specific temperature. From these runs a value "k" for the reaction velocity of azide rearrangement (as a unimolecular reaction) can be determined. Then from Equation 2, the azide rate of decomposition can be determined for any time period. A typical analytical run is given in the following paragraphs (see Table IV):

Table IV. Azotometer Run of Structure X

| ①<br>Clock<br>Time | ②<br>Elapsed<br>Min | ③<br>Accumulated<br>Gas Vol | ④<br>Blank | ⑤<br>Volume of<br>Nitrogen<br>③ - ④ | ⑥<br>Correction for<br>Normal Temp<br>and Press.<br>⑤ x 0.871 | ⑦<br>Conversion to<br>Weight in Mg<br>⑥ x 1.25 mg/cc | ⑧<br>Percent of Azide<br>Decomposed<br>100 x ⑦/18.3 |
|--------------------|---------------------|-----------------------------|------------|-------------------------------------|---|--|---|
| 2:47               | 0                   | 0                           | 0          | 0                                   | 0   | 0  | 0   |
| 3:10               | 23                  | 5.35                        | 0.4        | 4.95                                | 4.31  | 5.37   | 29.3  |
| 3:25               | 38                  | 9.25                        | 0.8        | 8.45                                | 7.36  | 9.18   | 50.2  |
| 3:40               | 53                  | 11.75                       | 1.2        | 10.55                               | 9.19  | 11.55  | 62.8  |
| 3:55               | 68                  | 13.80                       | 1.6        | 12.20                               | 10.63   | 13.15  | 71.9  |
| 4:10               | 83                  | 15.50                       | 2.0        | 13.50                               | 11.76   | 14.65  | 80.1  |

The effect of the starting time of 8 minutes (see Figure 8) is minimized by the determination of  $k$  on the basis of the half life of azide rearrangement:

$$\frac{dx}{dt} = -kx \quad (2)$$

where

$x$  = amount of azide in grams,

$t$  = time after start of azotometer run,

$k$  = reaction velocity of azide rearrangement.

$$\frac{dx}{x} = -kdt$$

$$\int_x^0 \frac{dx}{x} = -k \int_0^t dt \quad (3)$$

$$\ln x \Big|_x^0 = -kt \Big|_0^t .$$

when  $t = 0$ ,  $x = 1$ ; when  $x = 0$ ,  $t = \infty$ .

For half life:

$$\ln x \Big|_x^{\frac{x}{2}} = -kt \Big|_0^{\frac{t}{2}}$$

$$\ln \frac{x}{2} - \ln x = -k \left( \frac{t}{2} \right)$$

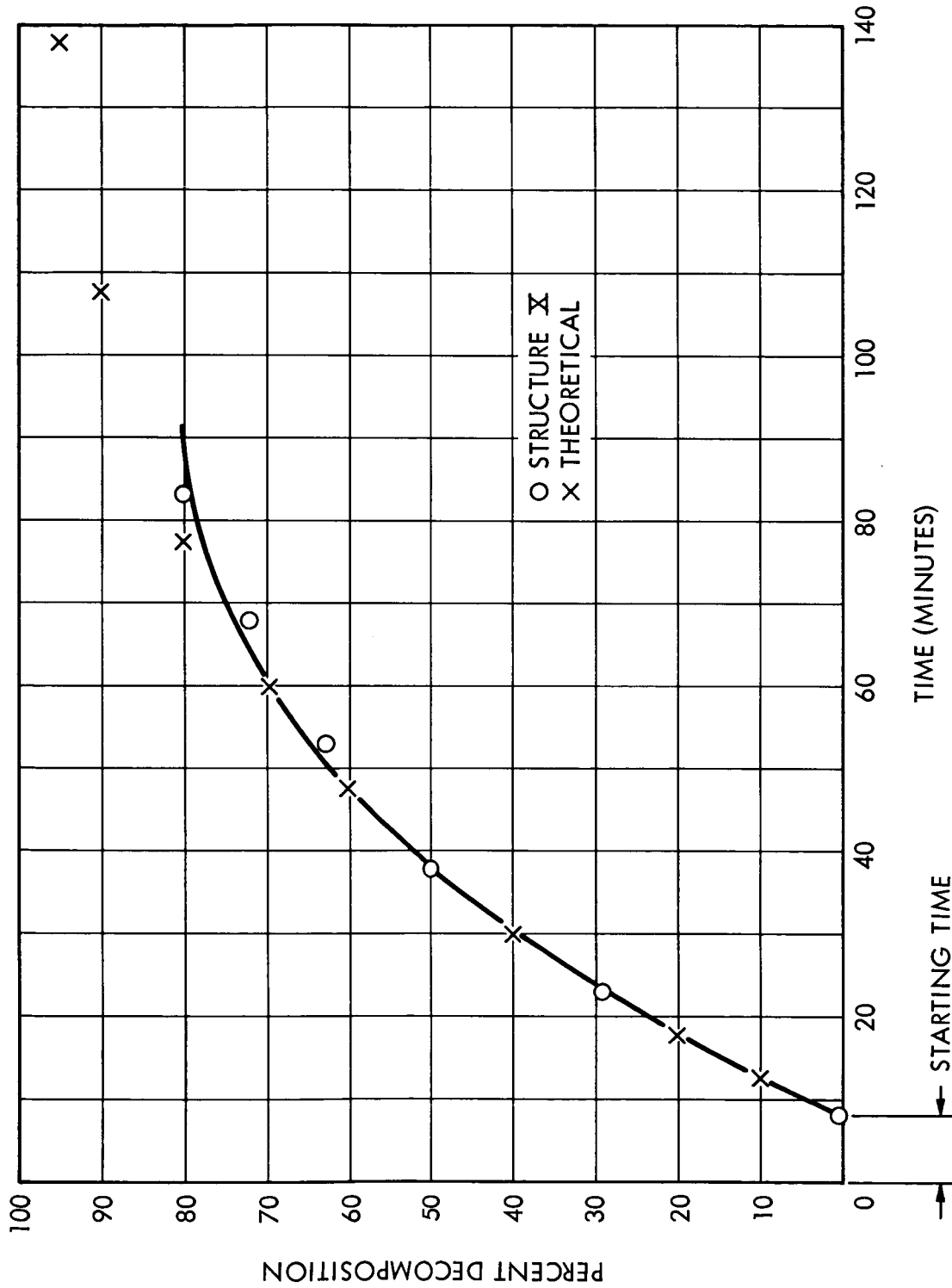


Figure 8. Percent of Azide Decomposition against Time  
(Azide Structure X at 193°F)

$$\ln \left( \frac{1}{2} \right) = -k \left( \frac{t}{2} \right)$$

$$-0.693 = -k \left( \frac{t}{2} \right).$$

$$\text{If } \left( \frac{t}{2} \right) = (38-8) = 30 \text{ (see Figure 8),}$$

$$k = \frac{0.693}{30} = 2.31 \times 10^{-2}.$$

The ordinate values for Figure 8 are obtained by solving for  $N_1$  in the following expression:

$$\int_0^{N_1} \frac{dn}{n} = -k \int_0^{t_1} dt,$$

where

$N_1$  = the value  $N$  from Equation 1

$$k = 2.31 \times 10^{-2}$$

$t_1$  = actual time minus starting time

and subtracting from 100, e. g., percent decomposition =  $(100 - N_1)$ .

The separation of experimental values from theoretical values at the higher percentage of decomposition is considered as possibly due to the impurities in the azide structure.

APPENDIX B. MEASUREMENT OF HEAT RELEASE  
FROM AZIDE REARRANGEMENT

A test apparatus has been assembled and calibrated to determine the heat of decomposition of candidate azide materials (see Figures 9, 10, and 11). The assembly is essentially a calorimeter which provides a means for controlling the initial or "triggering" temperature for the test material. The apparatus consists of a thin-walled glass test tube enclosed in a glass Dewar. Thermocouples placed in the test tube are connected to a chart recorder. The Dewar is connected to a vacuum pump. The space between the test tube and the Dewar inner wall is evacuated. The test tube surrounded by radiation shields (aluminized Mylar) and vacuum results in a low heat loss system.

Calibration of the system was accomplished by the method of mixtures. A solid specimen of known mass and specific heat was heated and lowered into the test tube containing an inert liquid (paraffin oil). The equivalent specific heat of the system is calculated by use of the following equation:

$$c_{cu} m_{cu} \Delta t_{cu} = c_s m_s \Delta t_s$$

(Heat lost by copper) = (Heat gained by system),

or

$$c_s = \frac{c_{cu} m_{cu} \Delta t_{cu}}{m_s \Delta t_s},$$

where

$c_s$  = equivalent specific heat of calorimeter (cal/gm °C),

$m_s$  = mass of inert fluid (grams),

$\Delta t_s$  = temperature change of fluid (°C),

$c_{cu}$  = specific heat of copper (cal/gm °C),



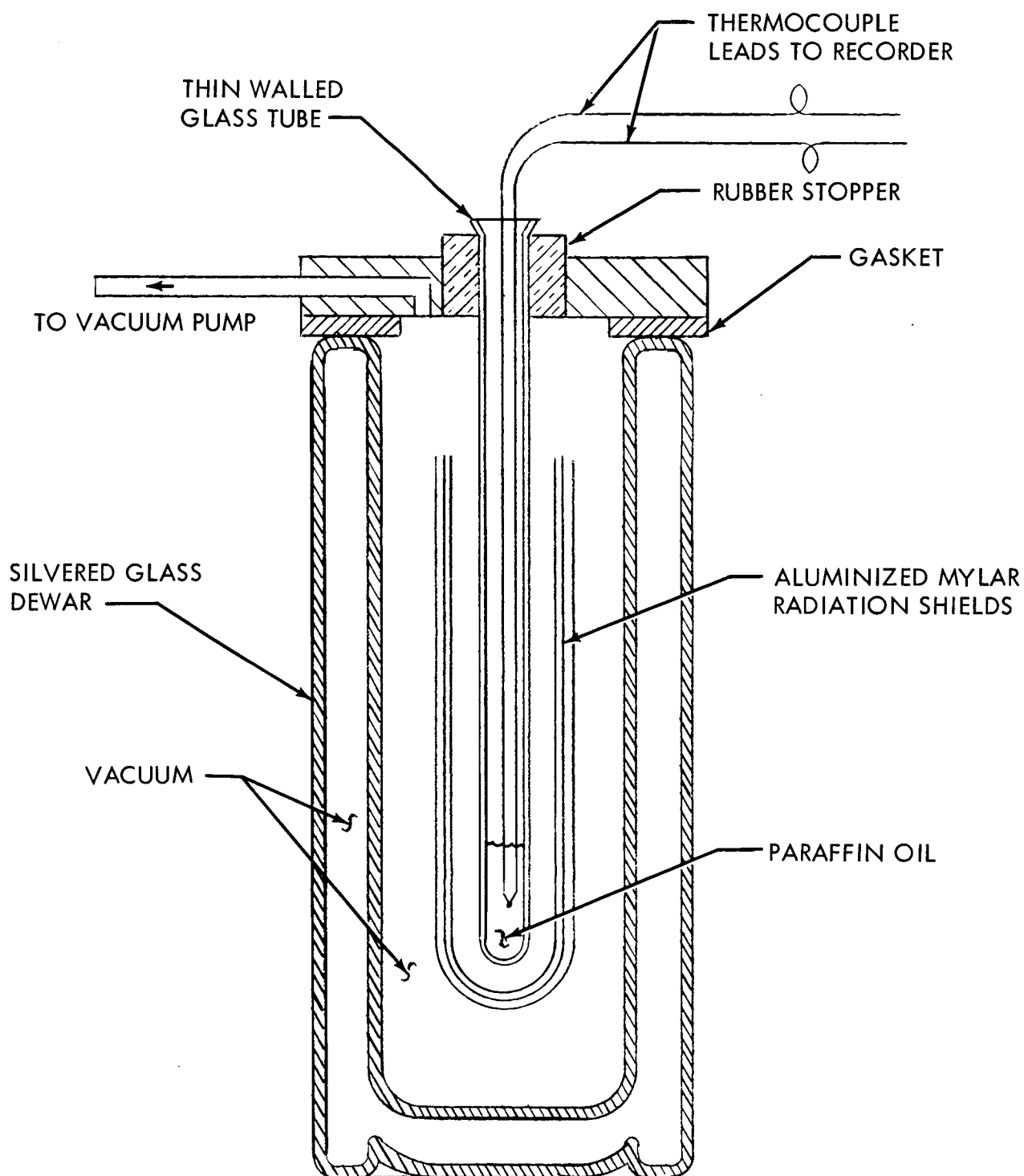


Figure 9. Sketch of Heat of Decomposition Apparatus

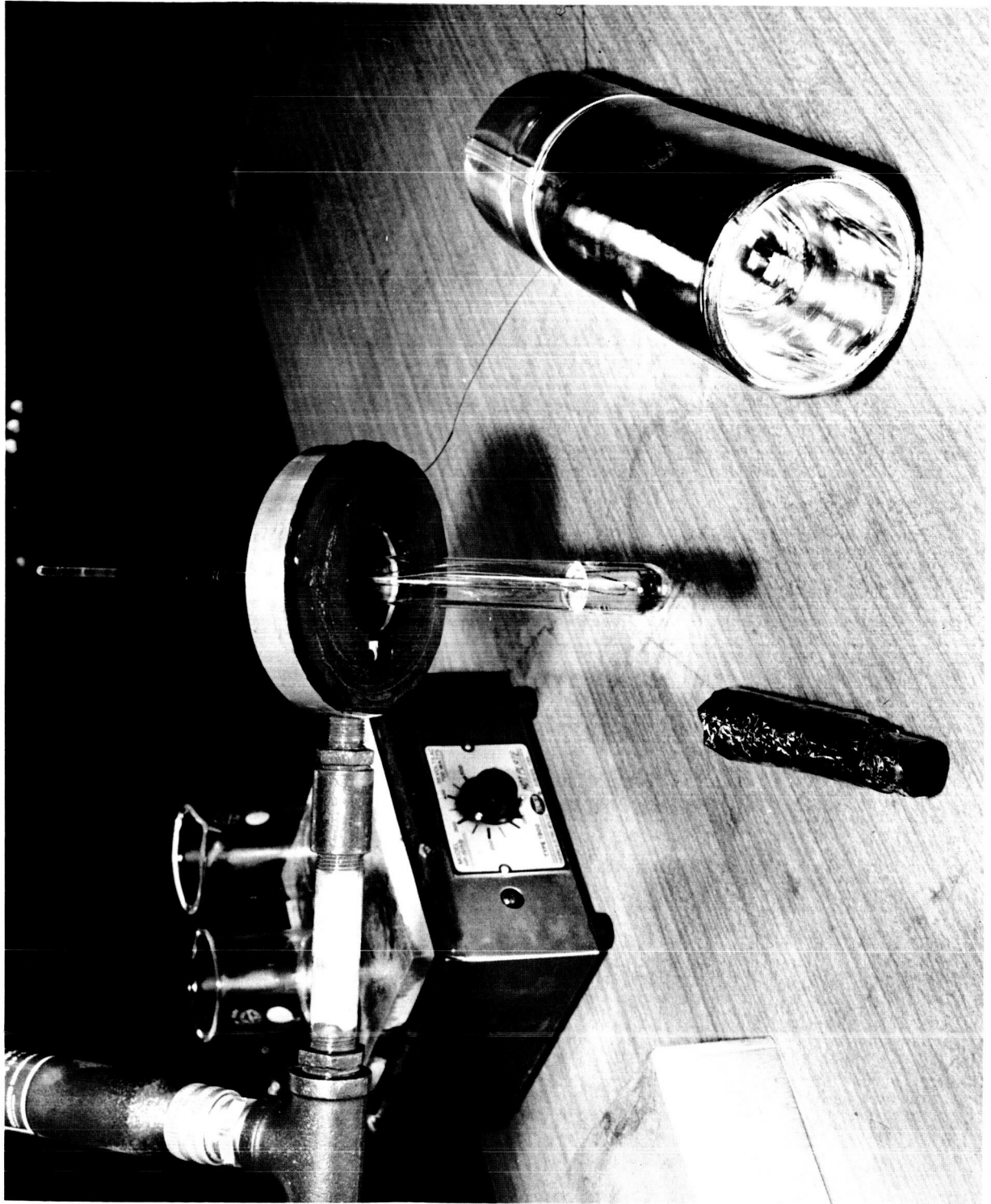


Figure 10. Heat of Decomposition Apparatus - Disassembled

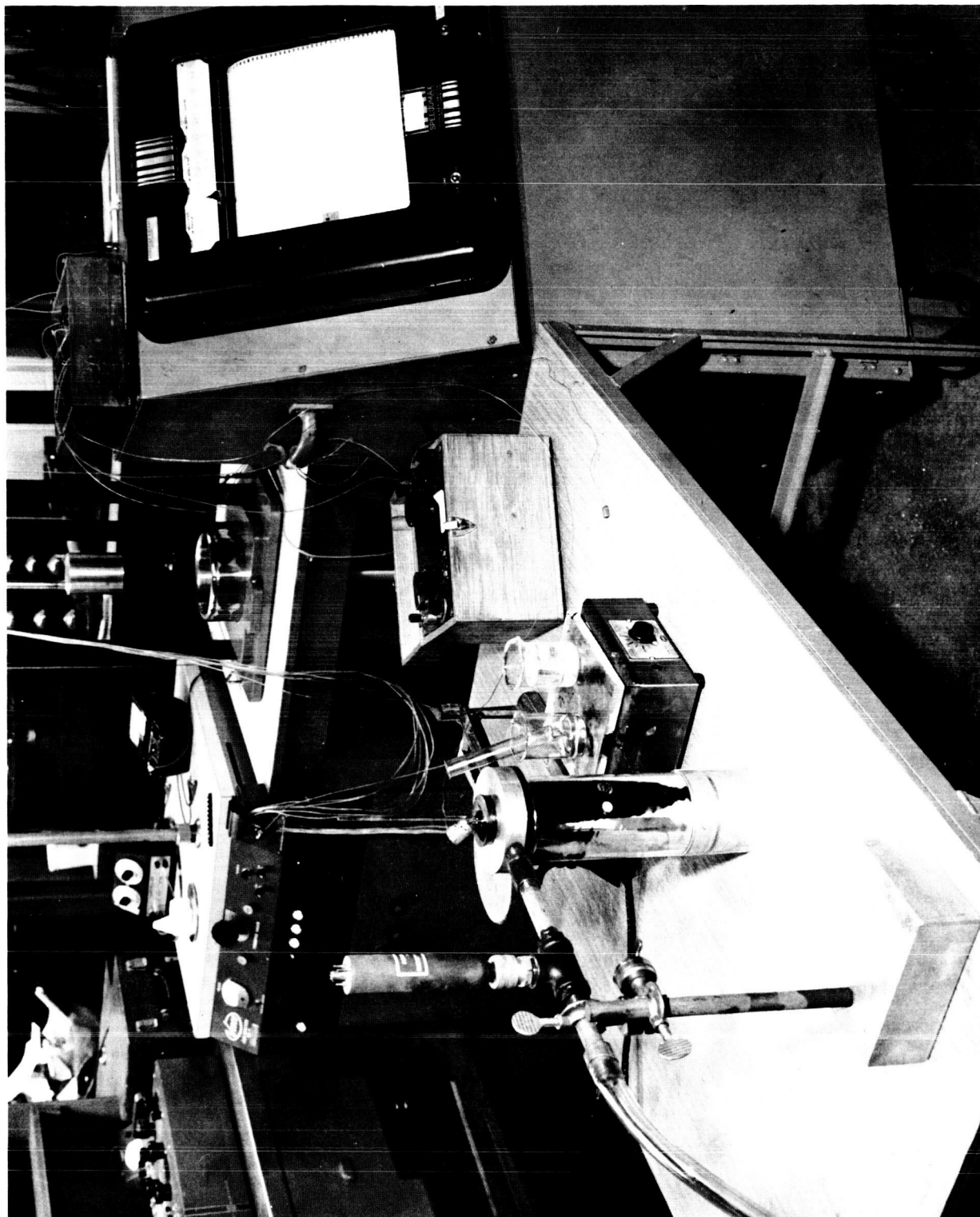


Figure 11. Heat of Decomposition Apparatus - Assembled

$m_{\text{cu}}$  = mass of copper specimen (grams),

$\Delta t_{\text{cu}}$  = temperature change of copper specimen ( $^{\circ}\text{C}$ )

The inert liquid (paraffin oil) was then heated and poured into the test tube. The cooling rate of the liquid was determined by the thermocouple and the recorder. When the temperature of the liquid dropped to the desired level, a copper specimen was lowered into the liquid. Temperature changes of the liquid and the copper specimen were recorded.

The determination of the heat of decomposition of the azide materials is conducted basically the same as described for the calibration except that a known quantity of azide supplies the added heat to the inert liquid instead of the copper specimen.

## APPENDIX C. SUBLIMATION TESTS

The sublimation tendency of the candidate precoat foam materials is being determined by the weight loss method. Precoat foam formulations are prepared and applied to the cups of the apparatus shown in Figures 12, 13, and 14. The cups are then subjected to a high-vacuum environment for a specified time interval after which one cup is removed and the weight loss determined with a minimum exposure to the atmosphere. The remaining cups are returned to the high-vacuum environment. After a specified time exposure, a second cup is removed and the weight loss determined. This procedure continues until a curve can be established for the rate of sublimation of the material.

Initial tests were performed at room temperature. More severe tests are performed with the material subjected to heat approaching the azide reacting temperature as well as the high vacuum.

A 4-inch diameter by 1/2-inch thick copper plate contains seven wells in which the copper specimen cups are placed. Temperature control is obtained manually for short-time runs by adjusting power to the electric heater with a variac. For long-duration tests, temperature is automatically controlled with a "Simplytrol" temperature controller. Temperature of the copper plate is sensed by thermocouples and is recorded on a strip chart recorder. Calibration tests were conducted to determine if the specimen cup temperature is the same as that of the copper plate. Since the tests are performed in a vacuum, good mechanical contact must exist to permit proper heat transfer. This has been accomplished by means of stainless steel wires (anchored to screws on the copper plate) acting as springs and exerting a small force against the specimen cups. Tests have shown that

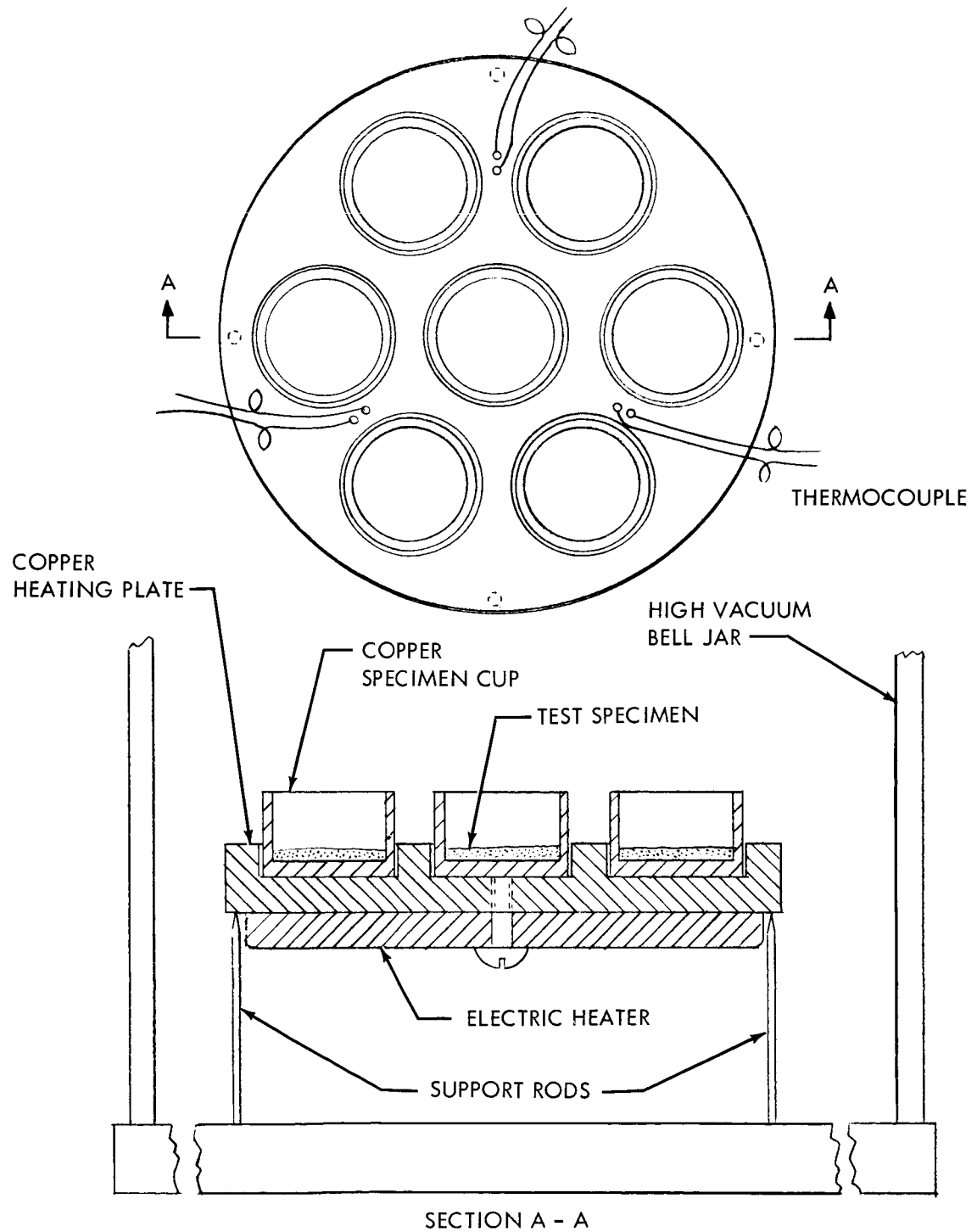


Figure 12. Sketch of Sublimation Test Apparatus

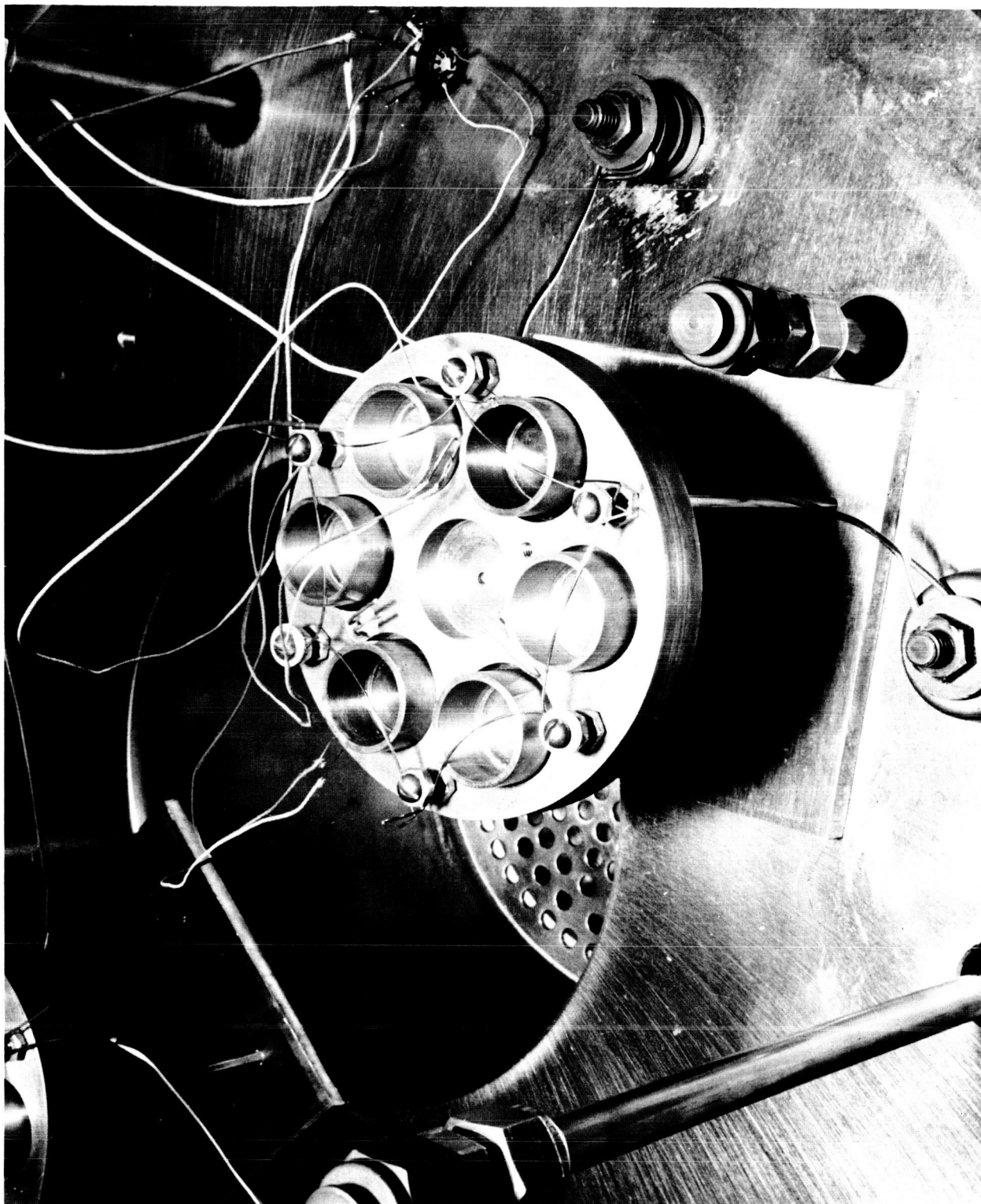


Figure 13. Closeup of Sublimation Test Apparatus



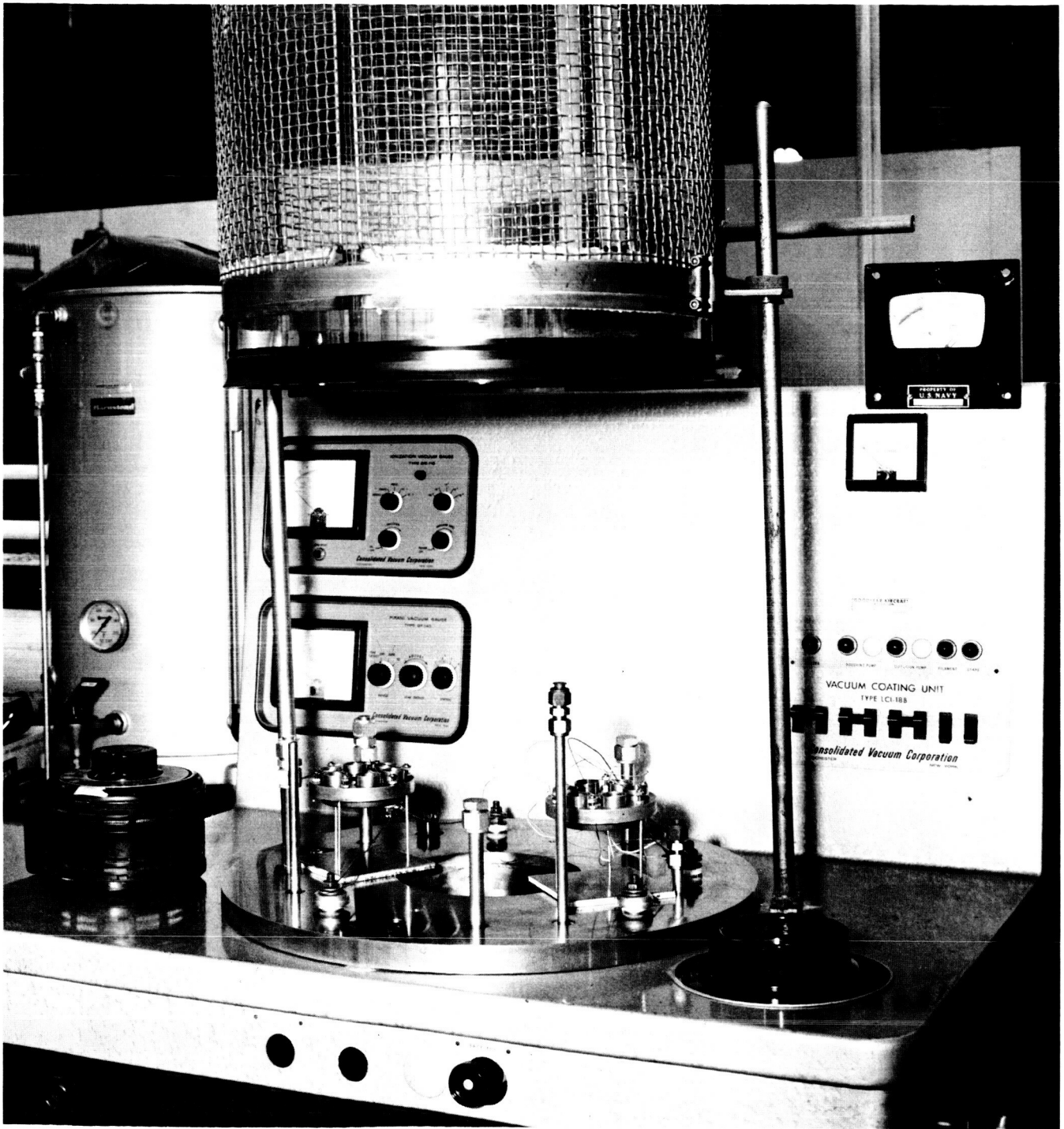


Figure 14. Sublimation Test Apparatus in Bell Jar Installation



specimen cup temperatures are within 2 °F of the copper plate temperature.

The procedure followed for conducting a sublimation test is as follows:

- (1) Weigh empty cups.
- (2) Weigh cups with sample material.
- (3) Condition in bell jar overnight at a pressure of from 10 to 50 microns.
- (4) Weigh samples.
- (5) Evacuate bell jar to  $10^{-5}$  torr.
- (6) Apply heat and retain pressure  $\leq 10^{-2}$  torr.
- (7) Weigh first sample after two hours.
- (8) If difference in weight is significant, weigh succeeding samples in one-hour intervals. If weight difference is not significant, weigh succeeding samples in intervals of  $\geq$  two hours.